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International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C08L 67/04

A1

(11) International Publication Number: WO 00/64975

(43) International Publication Date: 2 November 2000 (02.11.00)

(21) International Application Number: PCT/SE00/00696

(22) International Filing Date: 12 April 2000 (12.04.00)

(30) Priority Data:
9901517-4 27 April 1999 (27.04.99) SE

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(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
*With international search report.*
*In English translation (filed in Swedish).*

(54) Title: PROCESS FOR PRODUCTION OF AN ACRYLATE COMPOSITION

(57) Abstract

Process for production of an acrylate composition comprising at least one dendritic polyester acrylate oligomer and at least one acrylate monomer, said process comprising mixing at least one dendritic polyester, having one or more terminal hydroxyl groups and at least one alcohol, having one or more hydroxyl groups and a molecular weight of at most 2000. Obtained mixture is subsequently acrylated by reaction with at least one compound comprising at least one acrylic unsaturation yielding a reaction mixture comprising an acrylate composition comprising at least one dendritic polyester acrylate oligomer and at least one acrylate monomer, whereby said acrylate composition can be recovered from said reaction mixture.

# PROCESS FOR PRODUCTION OF AN ACRYLATE COMPOSITION

The present invention relates to a process for production of an acrylic composition comprising at least one dendritic polyester acrylate oligomer and at least one acrylate monomer.

Protective and decorative paints and lacquers, glues and other drying and curing compositions based on acrylic and methacrylic polymers meet with an increasing importance within a large number of applications. The increasing importance is substantially due to the utility and unique properties of said polymers, such as short curing times, excellent film properties, low or no amounts of solvents. Acrylic compositions for said and other applications often comprise a number of various components, such as one or more polyester acrylates, for example polyester acrylate oligomers and polymers, and one or more functional monomers, for example esters of an alcohol and an acrylic acid. Functional monomers work, besides being monomers, also as viscosity reducing diluents for said oligomers and polymers.

The properties of an acrylate, such as film forming, curing, drying and the like, are determined by for instance the molecular weight and molecular structure as well as the chemical and physical structure of said acrylate. Dendritic macromolecules, such as dendritic polyesters, have gained a major interest as said molecules in various applications normally exhibit many unique properties not possible to obtain using conventionally branched and linear products, as disclosed in the Swedish patent nos. 468 771, 502 634, 503 342, 503 622, 504 879 and 509 240 as well as in the International Patent Applications WO 97/23538 and WO 97/23539, all teaching various types of dendritic polyesters with and without chain termination as well as the use and properties of said polyesters in applications such as binders, thermosets, thermoplastics and lubricants. Dendritic polymers comprise hyperbranched species having a certain degree of polydispersity and monodiperse dendrimers. Dendritic molecules are further discussed in for instance "Dendritic Molecules - Concepts, Syntheses, Perspectives" by G.R. Newkome, C.N. Moorefield and F. Vögtle, 1996, VCH Verlagsgesellschaft mbH, Germany. Acrylic esters and other acrylic polymers, oligomers and monomers as well as their properties are thoroughly discussed in available literature such as Kirk-Othmer, "Encyclopedia of Chemical Technology" - Wiley-Interscience Publication, 1980. vol. 1 pages 386-413 "Acrylic Ester Polymers" and "Chemistry & Technology of UV and EB Formulations for Coatings, Inks and Paints" by N.S. Allen, M.S. Johnson, P.K.T. Oldring and S. Salim; 1991 Selective Industrial Training Associates Ltd. London, UK.

Acrylic products having a well defined, tailor-made and/or unique structures can thus be produced by acrylation of dendritic polyesters having for instance one or more terminal hydroxyl groups. The unique structure of dendritic polyesters makes production of for instance acrylic oligomers having a high molecular weight and a high acrylic functionality combined

with a low viscosity in relation to the molecular weight, which is a desired relation in the production and use of for instance acrylic oligomers and monomers. Dendritic structures, including hyperbranched molecules and dendrimers, give furthermore a unique balance between for example film hardness, surface hardness, adhesion and flexibility. Problems have, however, occurred during acrylation and recovery of dendritic polyesters. A commonly used process during said recovery and refining often include water leaching of unreacted acrylic acid. The high molecular weight and the high polarity of dendritic polyesters tend in this context to yield stable or comparatively stable emulsions, which substantially obstruct said recovery and refining. It has, however, quite unexpectedly been found that said problem can be overcome or substantially reduced if a dendritic polyester, optionally partially chain terminated or functionalised, having at least one terminal hydroxyl group, prior to acrylation is diluted or mixed with at least one alcohol having at least one hydroxyl group and a molecular weight of at most 2000, such as 60-1500 or 100-1000, which alcohol preferably is liquid at a temperature of 20-50°C or yields liquid mixtures with said dendritic polyester at said temperature. Obtained mixture is subsequently acrylated using common and well known methods, such as reaction with at least one compound comprising at least one acrylic unsaturation. A reaction mixture comprising an acrylic composition comprising at least one dendritic polyester oligomer and at least one acrylic monomer is yielded in said acrylation. The acrylic composition can subsequently be recovered and refined by means of known methods, such as said water leaching, without formation of disturbing stable emulsions. Acrylation as well as recovery and refining are, furthermore, facilitated as the polyester/alcohol mixture normally has a viscosity being lower than included polyester.

Various embodiments of the process of the present invention comprise mixtures wherein the alcohol is a diol, such as an ethylene glycol, a 1,2- or 1,3-propylene glycol, a butanediol or a di, tri or polyglycol, for example a diethylene glycol, a triethylene glycol, a polyethylene glycol, a dipropylene glycol, a tripropylene glycol, a polypropylene glycol or a glycol polymer such as a polymer comprising one or more ethylene glycols and one or more propylene glycols. Further preferred embodiments include alcohols being reaction products between at least one 2-hydroxyalkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol or 2,2-di(hydroxyalkyl)-1,3-propanediol and at least one alkylene oxide at a molar ratio said 1,3-propanediol to said alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20 or being a reaction product between a dimer, trimer or polymer of said 1,3-propanediol and at least one alkylene oxide at a molar ratio said dimer, trimer or polymer to said alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20. Said reaction products can suitably be exemplified by alkoxylated, such as ethoxylated and/or propoxylated, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane and dipentaerythritol. The alcohol can furthermore and advantageously be a linear or branched alkanol, such as a $C_1$-$C_{24}$ alkanol or preferably a $C_4$-$C_{12}$ alkanol, such

as a butanol, a heptanol, a hexanol, an octanol, a nonanol, a decanol and/or a dodecanol, and/or be a 1,3-dioxane alcohol or a 1,3-dioxolane alcohol, such as a 5-hydroxy-1,3-dioxolane, a 5-hydroxy-1,3-dioxane, a 5-hydroxyalkyl-1,3-dioxane, a 5-alkyl-5-hydroxyalkyl-1,3-dioxane and/or a 5,5-di(hydroxyalkyl)-1,3-dioxane. Further suitable alcohols are found among reaction products between 1,3-dioxane alcohols or 1,3-dioxolane alcohols as disclosed above and at least one alkylene oxide at a molar ratio as previously disclosed. Alkoxylated 1,3-dioxane alcohols can be exemplified by for instance ethoxylated and/or propoxylated 5-hydroxymethyl-1,3-dioxane and 5,5-di(hydroxymethyl)-1,3-dioxane. Alkyl is in above disclosed embodiments preferably and independently $C_1$-$C_{12}$ alkanyl or $C_2$-$C_{12}$ alkenyl. The alkylene oxide is likewise preferably ethylene oxide, propylene oxide, butylene oxide, phenylethylene oxide (styrene oxide) or a mixture of two or more alkylene oxides.

The dendritic polyester, which is included in the mixture of the present process, is in preferred embodiments built up from a core molecule, having one or more hydroxyl or epoxide groups, and one or more dendrons bonded to said groups. A dendron comprises preferably two or more branching generations built up from at least one hydroxy and/or epoxy functional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxy functional monocarboxylic acid and/or at least one lactone. The dendritic polyester can alternatively be equal to said dendron. The dendritic polyester can furthermore be partially chain terminated or functionalised, whereby it has at least one terminal hydroxyl group, optionally in combination with one or more epoxide, alkenyl, amino, amide, aminoamide, thiol, anhydride, carboxyl, cyano, phosphate, phosphite, phosphin, suphate and/or sulphite groups or the like.

Embodiments of the process according to the present invention comprise at least dendritic polyester having a core molecule. Said core molecule is in said embodiments preferably a 1,3-propanediol, such as a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol or a dimer, trimer or polymer of a said 1,3-propanediol. Alkyl is preferably and independently $C_1$-$C_{12}$ alkanyl or $C_2$-$C_{12}$ alkenyl and alkoxy is, likewise preferably and independently, ethoxy, propoxy or butoxy comprising 1 to 50, such as 1 to 20, units of respective alkoxy. Said core molecules can suitably be exemplified by 2-butyl-2-ethyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane, anhydroennea-heptitol and dipentaerythritol and reaction products between a said di, tri or polyalcohol and at least one alkylene oxide, such as ethylene oxide, propylene oxide or butylene oxide, at a molar ratio alcohol to alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.

Preferred embodiments of the process according to the present invention furthermore comprise a dendritic polyester wherein one or more dendrons comprise at least one generation built up from at least one di, tri or polyhydroxy functional monocarboxylic acid. Said carboxylic acid can suitably be exemplified by dimethylolpropionic acid, α,α-bis(hydroxymethyl)butyric acid, α,α-bis(hydroxymethyl)valeric acid, α,α-bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid, α,α,α-tris(hydroxymethyl)acetic acid, citric acid and heptonic acid. A dendron can, furthermore, optionally comprise at least one generation built up from at least one monohydroxy functional monocarboxylic acid or lactone, which acid or lactone suitably can be exemplified by hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide, δ-valerolactone, β-propiolactone and ε-caprolactone.

The dendritic polyester included in the process of the present invention can furthermore in various embodiments be partially chain terminated through for instance reaction with at least one alkanyl, cycloalkanyl, alkenyl, cycloalkenyl, alkynyl or aryl compound, such as a mono, di, tri or polyfunctional carboxylic acid, which carboxylic acid suitably can be exemplified by saturated or unsaturated monocarboxylic acids and dicarboxylic acids having up to 24, such as 6-18, carbon atoms.

The dendritic polyester and the alcohol is, in the most preferred embodiments of the process of the present invention, prior to acrylation mixed in a weight ratio polyester to alcohol of between 90:10 and 10:90, such as between 25:75 and 75:25 or between 40:60 and 60:40.

Acrylation, recovery and refining of obtained polyester/alcohol mixture is suitably performed using methods well known from the literature, as for instance disclosed in Kirk-Othmer Encyclopedia of Chemical Technology - 1980 vol. 1, pages 386-413 "Acrylic Ester Polymers", Ullmanns Encyklopädie der technischen Chemie - 3:rd ed. 1953, Band 3, pages 78-81 "Acrylsäureester" and in Technical Information Leaflets nos. 0900-0912 issued by Perstorp Polyols, Sweden. The acrylation is preferably a direct reaction, such as esterification, with acrylic acid, methacrylic acid, crotonic acid (β-methacrylic acid) and/or a direct reaction with an anhydride and/or a halide corresponding to a said acrylic acid, preferably at a molar ratio hydroxyl groups to said acid, anhydride and/or halide of between 1:0.1 and 1:5, such as between 1:0.5 and 1:1.5. Further acrylic compounds suitable for acrylation of the polyester/alcohol mixture according to the present process include for example epoxide or anhydride functional acrylates and methacrylates such as glycidylmethacrylate.

The present invention is by below embodiment examples 1-6 further illustrated, whereby
- Example 1 shows preparation of an acrylic composition according to the invention and measurements of phase separation.

- Example 2 and 3 show a comparative acrylation outside the scope of the invention and evaluation results in comparison with Example 1.
- Example 4-6 show evaluations of products obtained in Examples 1 and 3.

**Example 1**

40.0 g of a dendritic polyester nominally having 16 terminal hydroxyl groups (Boltorn® H20, Perstorp Specialty Chemicals, Sweden), 160.0 g of a trifunctional polyalcohol (Polyol TP30™, Perstorp Specialty Chemicals, Sweden) were mixed and charged together with 163.8 g of acrylic acid, 10 drops of nitrobenzene, 0.5 g of methoxyphenol and 425 ml of toluene in a three-necked reaction flask provided with a magnetic stirrer, gas inlet, water trap (Dean-Stark), cooler and oil bath. Stirring and inlet of air was commenced and the solution was heated to 55°C and 3.27 g of methanesulphonic acid was subsequently charged. The reaction mixture was now heated to 90°C, at which temperature esterification water began to evaporate. The temperature was subsequently during 180 min. progressively raised from 90°C to 110°C. The reaction was allowed to continue at this temperature for a further 210 min. until water evaporation ceased. The reaction mixture was now cooled to room temperature.

The reaction mixture was at room temperature pored into a 2 l beaker provided with a magnetic stirrer and a pH electrode. The solution was under stirring neutralised by addition of 425 ml of 1% NaOH (aq) until a pH of 7.0 was obtained. The mixture was now pored into a 2 l separation funnel and the time till phase separation was measured. Complete separation of organic phase and water phase was obtained within 30 min. The water phase was removed and the organic phase was washed with 2 x 500 ml of water, including removal of water phase between washings. Phase separation was checked and complete separation was in both washings obtained within 30 min.

The washed organic phase was subsequently evaporated in a roll evaporator applying vacuum and allowing air to bubble through. An acrylated final product was recovered as a low viscous, clear and colourless liquid.

Obtained final product exhibited following product data:

| | |
|---|---|
| Conversion of OH groups to acrylate, mole-% | 94.5 |
| Final acid value, mg KOH/g | 0.75 |
| Viscosity, Brookfield, 23°C, mPas | 180 |
| Non-volatile content, % | 98.9 |

**Example 2 (comparative)**

250.0 g of a dendritic polyester nominally having 16 terminal hydroxyl groups (Boltorn® H20, Perstorp Specialty Chemicals, Sweden) was charged in a three-necked reaction flask provided with a magnetic stirrer, gas inlet, water trap (Dean-Stark), cooler and oil bath. The product was heated until a homogeneous melt was obtained. 178.6 g of acrylic acid, 17 drops of nitrobenzene, 0.9 g of methoxyphenol, 6.43 g of methanesulphonic acid and 300 ml of toluene were subsequently charged to said product. Stirring and inlet of air was commenced and the mixture was heated to 105°C, at which temperature esterification water began to evaporate. The temperature was subsequently progressively raised to 113°C and the reaction was allowed to continue at said temperature until water evaporation ceased. The reaction mixture was now cooled to room temperature.

The reaction mixture was at room temperature pored into a 2 l beaker provided with a magnetic stirrer and a pH electrode. The solution was under stirring neutralised by addition of 425 ml of 1% NaOH (aq) until a pH of 7.0 was obtained. The mixture was now pored into a 2 l separation funnel and the time till phase separation was measured. Complete separation of organic phase and water phase was obtained over night (> 12 h). The water phase was removed and the organic phase was washed with 2 x 500 ml of water, including removal of water phase between washings as above.

The organic phase was refined as in Example 1, whereby a final product was obtained as a viscous, transparent, yellowish product.

Obtained final product exhibited following product data:

| | |
|---|---|
| Conversion of OH groups to acrylate, mole-% | 95.1 |
| Final acid value, mg KOH/g | 5.4 |
| Viscosity, Brookfield, 23°C, mPas | 53 600 |
| Non-volatile content, % | 98.2 |

**Example 3 (comparative)**

A mixture of acrylated dendritic polyester according to Example 2 and a commercially available polyolacrylate based on ethoxylated trimethylolpropane (Sartomer SR 454™) was prepared and the viscosity and colour value of said mixture was determined.

20.0 g of dendritic acrylate according to Example 2 was weighed into a 100 ml glass beaker. 80.0 g of Sartomer SR454™ was added thereto. The products were mixed by stirring, whereby a pale yellowish liquid was yielded. The Temperature of the mixture was adjusted 23°C and the viscosity was determined by means of a Brookfield viscometer and compared to viscosity data for the product according to Example 1. The colour value of respective product was furthermore determined. Following data was obtained:

| Product | Viscosity, Brookfield, 23°C, mPas | Colour value, APHA |
|---|---|---|
| Example 1 | 180 | 127 |
| Example 3 | 200 | 898 |

Product according to the present invention exhibited a substantially lower viscosity. The product according to Example 1 exhibited, furthermore, a substantially lower colour value compared to product according to Example 3..

**Example 4**

Three lacquer formulations were prepared by addition of a commercially available photoinitiator (Darocure™ 1173, Ciba Geigy, Switzerland) to the product obtained in Example 1 and Example 3 and to a commercially available acrylate based on ethoxylated trimethylolpropane (Sartomer SR454™). Following lacquer formulations were obtained:

| | Prod. acc. Ex. 1 | Prod. acc. Ex. 3 | SR454 |
|---|---|---|---|
| Product, %-w/w | 96.0 | 96.0 | 96.0 |
| Darocure 1173, %-w/w | 4.0 | 4.0 | 4.0 |

**Example 5**

The three lacquers according to Example 4 were coated at a film thickness of 30 µm on glass panels and UV cured in a UV oven (Wallace Knight, 20 m/min, 240 mJ/m²) using 1, 2 and 4 passages through the oven. Obtained cured lacquer films were of a very good quality without failure and having a high surface gloss. The cured lacquer films were conditioned at 23°C and 50% relative humidity for 24 hours. The filmhardness was subsequently measured as König seconds (Ks) using a König pendulum.

Measured film hardness of the three lacquers:

| | Prod. acc. Ex 1 | Prod. acc. Ex 3 | SR454 |
|---|---|---|---|
| 1 passage, Ks | 109 | 105 | 40 |
| 2 passages, Ks | 134 | 142 | 138 |
| 4 passages, Ks | 151 | 152 | 145 |

Product according to the present invention (Example 1) exhibited very good reactivity and was equal in quality to Example 3. Furthermore, lacquer according to Examples 1 and 3 exhibited higher initial reactivity than SR454.

**Example 6**

A hydroxyfunctional dendritic polyester (Boltorn® H20, Perstorp Specialty Chemicals, Sweden) was mixed at 20 %-w/w with tripropylene glycol yielding below viscosity

Boltorn® H20, %-w/w: 20
Tripropylene glycol, %-w/w: 80

Viscosity, 23°C, mPas: 660

Above result evidences the excellent solubility of dendritic polyesters in various alcohols. Further suitable alcohols are for instance glycerol, ethoxylated glycerol and propoxylated glycerol, and other types of ethoxylated as well as propoxylated alcohols.

## CLAIMS

1. Process for production of an acrylate composition comprising at least one dendritic polyester acrylate oligomer and at least one acrylate monomer **characterised in**, that said process comprises mixing at least one, optionally partially chain terminated or functionalised, dendritic polyester, having at least one terminal hydroxyl group, with at least one alcohol, having at least one hydroxyl group and a molecular weight of at most 2000, and subsequently acrylating obtained polyester/alcohol mixture in a reaction with at least one compound comprising at least one acrylic unsaturation, whereby a reaction mixture comprising an acrylate composition comprising at least one dendritic polyester acrylate oligomer and at least one acrylate monomer is yielded and whereby said acrylate composition can be recovered from said reaction mixture.

2. Process according to Claim 1 **characterised in**, that said alcohol has a molacular weight of 60-1500, preferably 100-1000.

3. Process according to Claim 1 or 2 **characterised in**, that said alcohol is liquid at a temperature of 20-50°C or yields liquid mixtures with at least one dendritic polyester at said temperature.

4. Process according to any of the Claims 1-3 **characterised in**, that said alcohol is at least one diol, such as at least one ethylene glycol, 1,2- or 1,3-propylene glycol and/or butanediol.

5. Process according to Claim 4 **characterised in**, that said diol is at least one di, tri or polyglycol, such as at least one diethylene glycol, triethylene glycol, polyethylene glycol, dipropylene glycol, tripropylene glycol and/or polypropylene glycol.

6. Process according to any of the Claims 1-3 **characterised in**, that said alcohol is at least one reaction product between at least one 2-hydroxyalkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol and/or 2,2-di(hydroxyalkyl)-1,3-propanediol and at least one alkylene oxide, such as ethylene oxide, propylene oxide and/or butylene oxide, at a molar ratio said 1,3-propanediol to said alkylene oxide of between 1:0.2 and 1:50, preferably between 1:1 and 1:20.

7. Process according to any of the Claims 1-3 **characterised in**, that alcohol is at least one reaction product between at least one dimer, trimer or polymer of a 2-hydroxyalkyl-1,3-propanediol, 2-alkyl-2-hydroxyalkyl-1,3-propanediol and/or 2,2-di(hydroxyalkyl)-1,3-propanediol and at least one alkylene oxide, such as ethylene oxide, propylene oxide and/or butyleneoxid, at a molar ratio said dimer, trimer or

polymer of said 1,3-propanediol to said alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.

8. Process according to Claim 6 or 7 characterised in, that said alcohol is ethoxylated and/or propoxylated trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane and/or dipentaerythritol.

9. Process according to any of the Claims 1-3 characterised in, that said alcohol is at least one linear or branched alkanol, such as butanol, heptanol, hexanol, octanol, nonanol and/or decanol.

10. Process according to any if the Claims 1-3 characterised in, that said alcohol is at least one 1,3-dioxane alcohol or at least one 1,3-dioxolane alcohol, such as a 5-hydroxy-1,3-dioxolane, 5-hydroxy-1,3-dioxane, 5-hydroxyalkyl-1,3-dioxane, 5-alkyl-5-hydroxyalkyl-1,3-dioxane and/or 5,5-di(hydroxyalkyl)-1,3-dioxane.

11. Process according to any of the Claims 1-3 characterised in, that said alcohol is at least one reaction product between at least one 5-hydroxy-1,3-dioxane, 5-hydroxyalkyl-1,3-dioxane, 5-alkyl-5-hydroxyalkyl-1,3-dioxane and/or 5,5-di(hydroxyalkyl)-1,3-dioxane and at least one alkylene oxide, such as ethylene oxide, propylene oxide and/or butylene oxide, at a molar ratio said 1,3-dioxane to said alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.

12. Process according to any of the Claims 6-11 characterised in, that alkyl independently is $C_1$-$C_{12}$ alkanyl or $C_2$-$C_{12}$ alkenyl.

13. Process according to any of the Claims 1-12 characterised in, that said dendritic polyester is built up from a core molecule, having one or more hydroxyl or epoxide groups, and one or more dendrons bonded to said groups, said dendron comprising two or more branching generations built up from at least one hydroxy and/or epoxyfunctional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxyfunctional monocarboxylic acid and/or from at least one lactone.

14. Process according to Claim 13 characterised in, that said core molecule is a 1,3-propanediol, such as a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propanediol, a 2,2-di-(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol.

15. Process according to Claim 13 characterised in, that said core molecule is a dimer, trimer or polymer of a 2-alkyl-1,3-propanediol, a 2,2-dialkyl-1,3-propanediol, a 2-hydroxy-2-alkyl-1,3-propanediol, a 2-hydroxyalkyl-2-alkyl-1,3-propaneiol, a 2,2-di(hydroxyalkyl)-1,3-propanediol, a 2-hydroxyalkoxy-2-alkyl-1,3-propanediol or a 2,2-di(hydroxyalkoxy)-1,3-propanediol.

16. Process according to Claim 14 or 15 characterised in, that alkyl independently is $C_1$-$C_{12}$ alkanyl or $C_2$-$C_{12}$ alkenyl and that alkoxy independently is ethoxy, propoxy or butoxy comprising 1 to 50, such as 1 to 20, units of respective alkoxy.

17. Process according to Claim 13 characterised in, that said core molecule is 2-butyl-2-ethyl-1,3-propanediol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane, anhydroennea-heptitol or dipentaerythritol.

18. Process according to Claim 13 characterised in, that said core molecule is a reaction product between trimethylolethane, trimethylolpropane, pentaerythritol, ditrimethylolethane, ditrimethylolpropane or dipentaerythritol and at least one alkylene oxide, such as ethylene oxide, propylene oxide or butylene oxide, at a molar ratio alcohol to alkylene oxide of between 1:0.2 and 1:50, such as between 1:1 and 1:20.

19. Process according to any of the Claims 1-12 characterised in, that said dendritic polyester is a dendron comprising two or more branching generations built up from at least one hydroxy and/or epoxyfunctional carboxylic acid, having at least one carboxyl group and at least two hydroxyl and/or epoxide groups, and optionally one or more spacing generations built up from at least one monohydroxy or monoepoxyfunctional monocarboxylic acid and/or from at least one lactone.

20. Process according to any of the Claims 13-19 characterised in, that a dendron comprises at least one generation built up from at least one di, tri or polyhydroxyfunctional monocarboxylic acid, such as dimethylolpropionic acid, α,α-bis(hydroxymethyl)buryric acid, α,α-bis(hydroxymethyl)valeriic acid, α,α-bis(hydroxy)propionic acid, 3,5-dihydroxybenzoic acid, α,α,α-tris(hydroxymethyl)-acetic acid, citric acid and/or heptonic acid.

21. Process according to any of the Claims 13-20 characterised in, that a dendron comprises at least one generation built up from at least one monohydroxyfunctional monocarboxylic acid and/or at least one lactone, such as hydroxyvaleric acid, hydroxypropionic acid, hydroxypivalic acid, glycolide, δ-valerolactone, β-propiolactone and/or ε-caprolactone.

22. Process according to any of the Claims 1-21 **characterised in**, that said dendritic polyester is partially chain terminated by reaction with at least one alkanyl, cycloalkanyl, alkenyl, cycloalkenyl, alkynyl or aryl compound.

23. Process according to Claim 22 **characterised in**, that said dendritic polyester is partially chain terminated by reaction with at least one mono, di, tri or polyfunctional carboxylic acid, such as a saturated or unsaturated carboxylic acid having up to 24 carbon atoms.

24. Process according to any of the Claims 1-23 **characterised in**, that said dendritic polyester and said alcohol is mixed at a weight ratio polyester to alcohol of between 90:10 and 10:90, such as between 25:75 and 75:25 or between 40:60 and 60:40.

25. Process according to any of the Claims 1-24 **characterised in**, that said compound comprising at least one acrylic unsaturation is acrylic acid, methacrylic acid, crotonic acid or is a to said acid corresponding anhydride or halide.

26. Process according to Claim 25 **characterised in**, that acrylation is performed at a molar ratio hydroxyl groups to said acid, anhydride or halide of between 1:0.1 and 1:5, preferably between 1:0.5 and 1:1.5.

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 00/00696

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC7: C08L 67/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | WO 9317060 A1 (PERSTORP AB), 2 Sept 1993 (02.09.93) -- | 1-26 |
| A | WO 9613558 A1 (PERSTORP AB), 9 May 1996 (09.05.96) -- | 1-26 |
| A | WO 9619537 A1 (PERSTORP AB), 27 June 1996 (27.06.96) -- | 1-26 |
| A | Polym. Mater. Sci. Eng., Volume 77, 1997, Mats Johansson et al, "Hyperbranched aliphatic polyesters as base for thermoset resins" page 124 - page 125 -- | 1-26 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" erlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 11 August 2000 | 17 -08- 2000 |
| Name and mailing address of the ISA/<br>Swedish Patent Office<br>Box 5055, S-102 42 STOCKHOLM<br>Facsimile No. +46 8 666 02 86 | Authorized officer<br>Eva Johansson/ELY<br>Telephone No. +46 8 782 25 00 |

## INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SE 00/00696

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---|---|---|
| WO 9317060 A1 | 02/09/93 | AT 165609 T | 15/05/98 |
| | | AU 3653093 A | 13/09/93 |
| | | CA 2117486 A,C | 02/09/93 |
| | | DE 69214153 D,T | 10/04/97 |
| | | DE 69318295 D,T | 01/10/98 |
| | | EP 0597042 A,B | 18/05/94 |
| | | EP 0630389 A,B | 28/12/94 |
| | | SE 0630389 T3 | |
| | | ES 2115762 T | 01/07/98 |
| | | FI 931821 A | 22/04/93 |
| | | HK 1005487 A | 00/00/00 |
| | | JP 2574201 B | 22/01/97 |
| | | JP 6507512 T | 25/08/94 |
| | | JP 7504219 T | 11/05/95 |
| | | SE 468771 B,C | 15/03/93 |
| | | SE 9200564 A | 15/03/93 |
| | | US 5378886 A | 03/01/95 |
| | | US 5418301 A | 23/05/95 |
| WO 9613558 A1 | 09/05/96 | AU 3861195 A | 23/05/96 |
| | | SE 502634 C | 27/11/95 |
| | | SE 9403680 A | 27/11/95 |
| WO 9619537 A1 | 27/06/96 | AU 4320296 A | 10/07/96 |
| | | CA 2206004 A | 27/07/96 |
| | | EP 0799279 A | 08/10/97 |
| | | JP 10500730 T | 20/01/98 |
| | | SE 503622 C | 24/07/96 |
| | | SE 9404440 A | 22/06/96 |